XIII. "On a New Phosphite of Ethyl, $3C_4 H_5O, PO_3$." By A. W. WILLIAMSON, Ph.D., &c. Communicated by Dr. SHARPEY, Sec. R.S. Received June 15, 1854.

The following results were obtained by Mr. Railton in an investigation undertaken in connexion with the idea that the water of constitution discovered by Wurtz may be conceived as basic. The processes for preparing the compound are thus described by Mr. Railton.

1st. When three atoms of absolute alcohol are acted upon by one atom of $PCl_3$, this compound is formed. The alcohol is introduced into a retort which is connected with an apparatus for upward distillation, and the retort is surrounded with a freezing mixture. The terchloride is then added drop by drop, the whole is then gently heated for some time, the vapour being allowed to run back into the retort. It is now distilled and the portion which comes off between $140°$ C. and $196°$ C. collected and redistilled, that portion being preserved which boils between $188°$ and $191°$ C. The quantity of pure ether obtained by this process was not large, and there was left in the retort a considerable amount of $PO_3$ and other products, which on further heating evolved inflammable phosphuretted hydrogen.

2nd. This ether is obtained with the greatest facility from ethylate of soda and terchloride of phosphorus.

I introduce into a thirty ounce stoppered retort about a pint of ether, which must be perfectly free from alcohol and from water. The ethylate of soda is then added, and as much $PCl_3$ is taken as is necessary to form chloride of sodium and phosphite of ethyl. The ether is absolutely necessary, for without it, the action of the $PCl_3$ is so violent, as to set fire to the ethylate.

The $PCl_3$ is introduced into the mixture of ether and ethylate of soda through a long funnel, which is drawn to an extremely fine point, by which means it enters drop by drop into the mixture, thus avoiding the violent action which otherwise occurs.

The retort should be kept quite cool and frequently shaken. If these precautions are neglected considerable loss is experienced.

When the whole of the $PCl_3$ has been added, the ether is distilled off by a water-bath. The retort is then transferred to an oil-bath

which is gradually heated up to about 240° C. The whole of the distillate obtained by the oil-bath is collected in a dry receiver, and as it is prone to decomposition if distilled in air, it is distilled in an atmosphere of hydrogen, the portion which comes off at 188° C. is the phosphite of ethyl. I may here notice the remarkable fact, that this substance has two boiling points, as doubtless have many other bodies, if distilled under similar circumstances. In air it boils at 191° C. while, as I said before, it boils in hydrogen at 188° C. Its specific gravity is 1·075.

3rd. The reaction which occurs on the formation of this ether may be represented by the following formula:—

$$3NaO, C_4H_5O + PCl_3 = 3NaCl + 3C_4H_5O, PO_3.$$
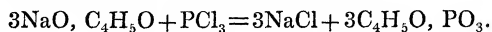
The carbon and hydrogen were estimated in the usual manner by oxide of copper, the phosphorus as follows. A weighed portion of the ether was introduced into a twelve ounce stoppered bottle; concentrated nitric acid was poured upon it, and the bottle allowed to stand in a warm place, loosely stopped, for several days. When nitrous fumes no longer appeared, the oxidation of the phosphorous acid was deemed to be complete. The acid liquid was then saturated with ammonia, some chloride of ammonium and sulphate of magnesia then added, and the mixture well shaken. It was allowed to stand for some time, when a precipitate of phosphate of magnesia and ammonia was formed; this was washed, dried, and ignited, and the amount of phosphorus calculated from the result. These are the results.

| Grms. | | $CO_2$ | HO | $2MgO, PO_5$ |
|---|---|---|---|---|
| ·2405 ether gave | | ·3784 and | ·1920 | ,, |
| ·5115 | ,, | ·8047 and | ·4155 | ,, |
| ·4513 | ,, | ,, | ,, | ·302 |
| ·4110 | ,, | ,, | ,, | ·278 |

From these results the following per centages are calculated.

| | Required. | Found. | |
|---|---|---|---|
| $C_{12}$ | 43·11 | 42·91 | 42·89 |
| $H_{15}$ | 8·98 | 8·87 | 9·03 |
| P | 19·16 | 18·92 | 19·10 |
| $O_6$ | 28·75 | 29·30 | 28·98 |
| | 100 | 100 | 100 |

These results being satisfactory as regards the formula, the density of the vapour was then ascertained and found to be in strict accordance with theory. The method of taking the vapour densities of bodies liable to oxidation was described by me about twelve months ago, in the Chemical Society's Quarterly Journal. It was used in the following experiments.

1st. Weight of globe filled with air at 53° F. and 30·2 in. barometer, 188·213 grs.

Weight of empty globe, 186·313 grs.

Weight of globe and vapour at 521° F. and 30·3 in. barometer, 192·387 grs.

Capacity of globe at 60° F., 6·00 cub. in.

Residual hydrogen ·05 cub. in.

Capacity of globe at 521° F., 6·40 cub. in.

Six cubic inches of air at 53° F. and 30·2 in. barometer, become at 60° F. and 30 in. barometer 6·12 cub. in., and weigh 1·90 grs.

·05 cub. in. hydrogen at 60° F. become ·094 cub. in. at 521° F., and weigh ·002 grs.

6·40 — ·094 = 6·306 cub. in. vapour at 521° F., which at 60° F. and 30 in. barometer = 3·376 cub. in.

Hence 192·387 — ·002 = 192·385 — 186·313 = 6·072 grains, the weight of 3·376 cub. in. vapour.

$$100 \text{ cubic inches.. } = 179·86 \text{ grs.}$$
$$100 \text{ cubic inches air} = 31·01 \text{ grs.}$$

The density is therefore 5·800, from which it appears that its combining measure is four volumes.

Density by calculation = 5·763.

A second experiment gave 5·877.

This substance has a highly offensive odour, it burns with a bluish white flame, is soluble in water, alcohol, and ether, and is slowly decomposed in contact with air.

On boiling phosphite of ethyl with concentrated solution of baryta, in water, it is decomposed into alcohol and a salt which varies according to the amount of baryta used. If one atom of the ether be treated with one of baryta, a crystallized salt is produced on evaporation, the carbon and hydrogen in which are, according to an analysis I have just completed.

|  | Found. | Required. |
|---|---|---|
| Carbon .... | 20·354 | 24·158 |
| Hydrogen .. | 5·356 | 5·050 |
| Baryta .... | 36·880 | 37·090 |

In that marked 'required' I have supposed the salt to bear the following formula and to be completely anhydrous, $2C_4H_5O$, BaO, $PO_3$, but if we suppose that four atoms of water are present in the salt analyzed, the relation will stand thus

| Found. | Required. |
|---|---|
| 20·354 | 20·453 |
| 5·356 | 5·540 |

The formula would then be $2C_4H_5O$, BaO, $PO_3 + 4HO$.

When two atoms of baryta are made to act upon one atom of the ether, a salt is obtained which does not crystallize, and it may be evaporated in air without sensible decomposition. This salt is perfectly neutral to test paper; when dry it is a white friable deliquescent mass, the formula of which will be $C_4H_5O$, 2BaO, $PO_3$. If an excess of baryta is used, a white salt is thrown down on boiling, which I suppose to be HO, 2BaO, $PO_3$.

I have prepared another compound with three equivalents of amyle. This was obtained from amylate of soda by an analogous process to that described for the phosphite of ethyl.

Analysis has pointed out the formula $3C_{10}H_{11}O$, $PO_3$. Like phosphite of ethyl it is easily decomposed on being heated in air; heated in hydrogen it is more stable and then boils at 236° C. It is soluble in ether and in alcohol, but only slightly soluble in water.